

Dimer phases in quantum antiferromagnets with orbital degeneracy

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We study and solve the ground-state problem of a microscopic model for a family of orbitally degenerate quantum magnets. The orbital degrees of freedom are assumed to have directional character and are represented by static Potts-like variables. In the limit of vanishing Hund's coupling, the ground-state manifold of such a model is spanned by the hard-core dimer (spin singlet) coverings of the lattice. The extensive degeneracy of dimer coverings is lifted at a finite Hund's coupling through an order-out-of-disorder mechanism by virtual triplet excitations. The relevance of our results to several experimentally studied systems is discussed.

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Isotropic quantum spin systems in dimensions higher than one have typically magnetically long-range ordered ground states and thus gapless spin excitations. This picture may, however, fail for so-called frustrated antiferromagnets, which have extensively degenerate classical ground states [1]. In such systems exotic quantum phases without long-range magnetic order can emerge as the true ground states. Spin systems can be frustrated by the geometry of the lattice or by the presence of competing interactions. In this letter, we discuss another scenario in which frustration of spin interactions is induced by the presence of additional electronic degrees of freedom, such as orbital degeneracy. A possibility of formation of orbitally driven magnetically disordered states has been suggested within various coupled spin-orbital models [2, 3, 4, 5].

Here we consider a generalization of the spin-orbital model of Ref. [4] to a wide class of lattices in arbitrary dimensions. We study and solve the ground-state problem for this model. We find remarkably that orbital degeneracy drives the spin degrees of freedom into an extensively degenerate manifold of spontaneously dimerized states. We demonstrate that various types of valence bond crystal (VBC) states can be selected by an order-out-of-disorder mechanism due to virtual triplet excitations. We motivate our study by several experimentally discovered spin gapped systems and discuss the relevance of our results to these materials.

The model.— The model is defined on an arbitrary lattice with links aligned along z distinct directions. We assume that at each lattice site there are z orbitally degenerate orthogonal levels such that each of them has hopping amplitudes only along the corresponding direction [6]. We further assume that, due to the strong on-site repulsion U , the system is in the Mott insulating state with exactly one electron per lattice site. The on-site repulsion also contains a small Hund's coupling J_H penalizing virtual processes with spin-zero state of a doubly occupied site. Such a model has experimental realizations on different lattices (see our discussion in the corresponding section). To the lowest order in t/U , where t is the hop-

ping amplitude (assumed to be the same for all links and corresponding orbitals), it leads to an effective Kugel-Khomskii-type Hamiltonian [7]. Since second-order virtual processes locally conserve orbital flavors, the orbital degrees are static Potts-like variables. The effective spin-orbital Hamiltonian for such a system takes the form [4]:

$$H = J \sum_{\langle ij \rangle} \left\{ [\vec{S}_i \cdot \vec{S}_j - \frac{1}{4}] O_{ij} - [\zeta + \eta \vec{S}_i \cdot \vec{S}_j] \tilde{O}_{ij} \right\} \quad (1)$$

where the sum is taken over pairs of nearest-neighbor (NN) sites. To the leading order in J_H/U , the coupling constants are given by $J \approx 4t^2/U$, $\eta \approx J_H/(2U)$, and $\zeta \approx \frac{1}{4}$. The small dimensionless parameter η characterizes the effective strength of the Hund's coupling. The full expressions for the coupling constants in terms of t , U , and J_H can be easily obtained from the exchange energies given in Ref. 4. For our further analysis, it will be important that $\zeta \geq \frac{1}{4}$ for all values of the Hund's coupling.

The first term of the Hamiltonian (1) describes the antiferromagnetic (AF) coupling between NN spins and is active when both ends of the link are occupied by the orbitals corresponding to the link direction. If α_{ij} denotes the “color” corresponding to the direction of the link ij , the operator O_{ij} is defined as $O_{ij} = \delta_{\sigma_i, \alpha_{ij}} \delta_{\sigma_j, \alpha_{ij}}$ where δ is the Kronecker symbol, and $\sigma_i = 1, \dots, z$ is the Potts-like variable for orbital flavor at the site i . The second term corresponds to the situation when on the bond ij only one orbital is of the color α_{ij} . The corresponding projector operator is $\tilde{O}_{ij} = \delta_{\sigma_i, \alpha_{ij}} [1 - \delta_{\sigma_j, \alpha_{ij}}] + \delta_{\sigma_j, \alpha_{ij}} [1 - \delta_{\sigma_i, \alpha_{ij}}]$.

For further analysis it is convenient to rewrite the Hamiltonian as the sum of three terms (in the units of J):

$$\begin{aligned} H &= H_{\text{AF}} + H_{\text{FM}} + E_0, \\ H_{\text{AF}} &= \sum_{\langle ij \rangle} [\vec{S}_i \cdot \vec{S}_j + (2\zeta - \frac{1}{4})] O_{ij}, \\ H_{\text{FM}} &= -\eta \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j \tilde{O}_{ij}, \end{aligned} \quad (2)$$

and E_0 is a static energy depending on the on-site “color” variables, but not on the dynamic spin degrees of freedom. It counts the number of matches between the colors of the link and one of its ends: $E_0 = -\zeta \sum_{i,j} \delta_{i,\alpha_{ij}}$.

This model can be solved exactly in the case of zero Hund’s coupling $\eta = 0$ on most commonly considered lattices (see the following section), and a further perturbative analysis at finite η is possible on many lattices, including the triangular and square lattice (see the corresponding section).

Zero Hund’s coupling.— We start our analysis from the limit of zero Hund’s coupling $\eta = 0$. In this limit, we show that the ground state is extensively degenerate and is described by dimer coverings of the lattice.

The term E_0 in the Hamiltonian only depends on the static orbital variables (colors). The antiferromagnetic term H_{AF} is active only on the links whose colors match those at both their ends. The active AF bonds thus form non-intersecting linear chains (Fig. 1, left). The longer is the chain, the more energy can be gained from the AF spin interaction. However, for each AF link we pay a positive energy ($2\zeta - \frac{1}{4} \geq 1/4$ (the second term in H_{AF})). We can prove that under these conditions the minimal possible AF energy is achieved when all AF chains are dimers. A proof follows from the variational estimate on the ground-state energy of the M -site AF Heisenberg chain with open ends: $E_M \geq \frac{1}{4} - \frac{M}{2}$, with the equality attained only at $M = 2$. [This estimate is, in turn, obtained by dividing the chain into shorter overlapping sub-chains of lengths two and three with exactly known energies $E_2 = -3/4$ and $E_3 = -1$.]

Therefore, at zero Hund’s coupling $\eta = 0$, the ground-state coloring of vertices corresponds to a dimer covering of the lattice (Fig. 1, right), provided that this dimer covering simultaneously minimizes E_0 . The minimization of E_0 is, for example, always possible for lattices where each site has equal valencies for all colors of outgoing links. This condition is satisfied for most well-known lattice types: triangular, square (cubic), kagomé, pyrochlore, checkerboard, hexagonal, etc. In addition, dimer coverings minimizing E_0 may also exist for other exotic lattices not satisfying the equal-color-valency constraint.

The dimer coverings corresponding to the ground state must obey an additional “no-chain” constraint: no two neighboring dimers can lie on the same line (otherwise they form a longer AF chain which is energetically unfavorable). Even with this constraint, the entropy of such dimer coverings remains extensive for most commonly considered lattices. Thus we conclude that, on such lattices, the model is in the dimer-liquid state at zero Hund’s coupling.

Order out of disorder by triplet fluctuations.— We now introduce a finite value of Hund’s coupling $\eta > 0$ and show that it lifts the extensive degeneracy of dimer coverings by triplet fluctuations. The Hund’s coupling produces a ferromagnetic term H_{FM} active only on links

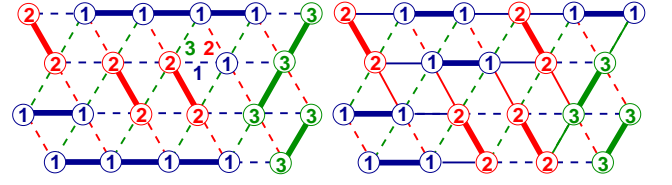


FIG. 1: (Color online) Left: A possible orbital pattern and the corresponding decoupled AF chains on the triangular lattice, in the limit of zero Hund’s coupling. The numbers label the three bond directions and the occupied orbitals on sites. Right: An example of the dimer covering minimizing the energy at zero Hund’s coupling. Thick (thin) solid lines denote AF (FM) intra-(inter-)dimer bonds, respectively.

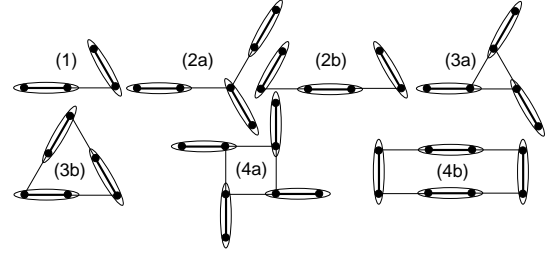


FIG. 2: Examples of topologically nonequivalent linked clusters.

with exactly one end matching the link color. Given a dimer covering from the previous consideration, the FM bonds correspond to the “legs” of dimers: adjacent links along the dimer direction (Fig. 1, right). We assume that the Hund’s coupling is small $\eta \ll 1$ and treat it perturbatively. A convenient method to build a perturbative expansion is to rewrite the FM coupling between two ends of dimers i and j in the basis of triplet excitations on those dimers [8]. At each dimer, we introduce three triplet excitations $t_{i,\alpha}^\dagger$ characterized by the spin polarization $\alpha = x, y, z$. Those triplet excitations may be treated as hard-core bosons, and the AF part of the Hamiltonian is written (in the units of J) as $H_{\text{AF}} = \sum_{i,\alpha} t_{i,\alpha}^\dagger t_{i,\alpha}$. The FM part of the Hamiltonian H_{FM} is treated as a perturbation and is written as the sum of the three contributions

$$\begin{aligned} H_1(i, j) &= -2\lambda m_i m_j \left[t_{i,\alpha}^\dagger t_{j,\alpha}^\dagger + t_{i,\alpha}^\dagger t_{j,\alpha} + h.c. \right] \\ H_2(i, j) &= 2\lambda \left[i\epsilon_{\alpha\beta\gamma} m_j t_{j,\alpha}^\dagger t_{i,\beta}^\dagger t_{i,\gamma} + [i \leftrightarrow j] + h.c. \right] \\ H_3(i, j) &= 2\lambda \epsilon_{\alpha\beta\gamma} \epsilon_{\alpha'\beta'\gamma'} t_{i,\beta}^\dagger t_{i,\gamma}^\dagger t_{j,\beta'}^\dagger t_{j,\gamma'}, \end{aligned} \quad (3)$$

where $m_i = \pm 1$ is a phase factor depending on the orientation of the singlet wave function on the dimer [8]. We also introduce $\lambda = \eta/8$, to simplify combinatoric coefficients.

A convenient way to analyze perturbative corrections is provided by the linked-cluster expansion [9]. The weak inter-dimer coupling H_{FM} is treated as a perturbation, and the correction to the ground-state energy may be written as a sum over all distinct linked clus-

ters $\Delta E = \sum_{\mathcal{C}} N_{\mathcal{C}} E_{\mathcal{C}}$. Here $N_{\mathcal{C}}$ is the number of ways the cluster \mathcal{C} can be embedded in the lattice with a given dimer covering and $E_{\mathcal{C}}$ is the perturbative contribution to the energy from the cluster \mathcal{C} (given by a power series in λ). Examples of topologically distinct clusters are presented in Fig. 2. Note that the leading contribution to $E_{\mathcal{C}}$ from tree-like clusters with n FM links is of order λ^{2n} [the clusters (1), (2a), and (2b) in Fig. 2], while loop clusters with n links [the clusters (3a), (3b), (4a) and (4b)] contribute to the order λ^n . The actual calculation of $E_{\mathcal{C}}$ involves lengthy combinatorial analysis of possible virtual processes and will be reported elsewhere. Here we just present the results of those calculations in application to the triangular and square lattices.

The leading perturbative contribution comes from the cluster (1) and is given by $E_{(1)} = -6\lambda^2(1 - 2\lambda + \lambda^2 + \dots)$. However, the total number of such clusters is independent of the dimer covering (it is equal to the number of interdimer bonds, *i.e.*, twice the number of dimers), therefore the degeneracy is not lifted to this order.

On the triangular lattice, the degeneracy is lifted to the leading order by the contributions from the cluster types (3a) and (3b) in Fig. 2. The cluster (3a) generates a non-frustrated FM coupling while the cluster (3b) is frustrated. The contributions of these two clusters differ in sign, $E_{(3a)} = -E_{(3b)} = -36\lambda^3$, to the leading order in λ . Thus, on the triangular lattice, the ground state should maximize the number of (3a) type clusters and minimize the number of (3b) type clusters. We prove that such an optimization leads to a dimer crystal shown in Fig. 3 (left panel). It provides the maximal density $N/5$ (N is the number of sites) of (3a) type clusters and no (3b) clusters. The unit cell of such a crystal contains 20 sites, and its degeneracy is 60-fold. A proof of crystallization may be performed by dividing the triangular lattice into edge-sharing hexagons composed of six triangles each. On a hexagon, we can place at most one triangular loop of a cluster (3a). A hexagon which has one of its edges shared by a triangular loop placed on an adjacent hexagon can not itself host a triangular loop. An empty hexagon can have at most two such edges (furthermore, they must be non-parallel and disconnected). To achieve the maximal density of triangular loops, we start with a three-hexagon cluster composed of an empty hexagon **B** sharing two edges with the triangular loops on the adjacent hexagons **A** and **C** (Fig. 3, the letters mark the centers of hexagons). Then the hexagon **D** must also be empty and, moreover, it may have at most one edge shared by a triangular loop (on the hexagon **E**). One can show that the maximal density of (3a) clusters is achieved by a close-packed covering of the triangular lattice by five-hexagon clusters of the type **A-E**. Now starting from one such cluster and choosing different possible divisions of the lattice into hexagons one can verify that the corresponding dimer covering is unique and periodic, as shown in Fig. 3 (left panel).

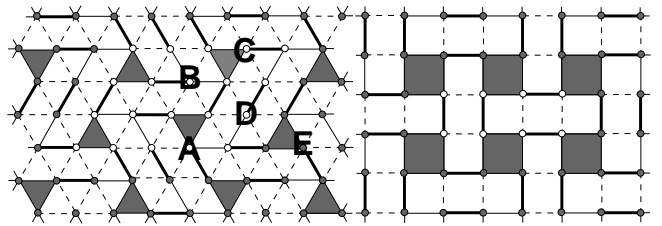


FIG. 3: Left: The ground state dimer covering of a triangular lattice. The triangular loops are explicitly shown as dark triangles. A possible choice of an unit cell is shown by open circles. Right: The ground state dimer covering of a square lattice. The length-four loops are shown as dark squares and white rectangles.

On the square lattice, a similar analysis needs to be done to the order λ^4 , since length-three loop clusters are not possible. At this order, the contributions come from the length-two clusters (2a) and (2b) and from the length-four loops (such as (4a) and (4b)), see Fig. 2 (other length-four loop clusters are also possible, but not shown). The clusters (2a) and (2b) have different contributions: $E_{(2a)} = 12\lambda^4$ and $E_{(2b)} = -20\lambda^4$. All length-four loop clusters involve unfrustrated FM couplings and contribute the same energy $E_{(4)} = -120\lambda^4$. With those cluster energies, we can prove that the resulting dimer covering forms a crystal shown in Fig. 3 (right panel). The proof is based on the observation that the energy gain from length-four loop clusters is much larger than the scale of energy optimization between (2a) and (2b) type clusters. Therefore, an optimal configuration should involve as many length-four loops, as possible (each FM link should belong to two such loops). Under this condition, an optimization of the energy contribution from clusters (2a) and (2b) leads to the crystal structure shown in the figure. Its unit cell contains 8 lattice sites, and the degeneracy is 8-fold.

On other lattices, we expect that virtual triplet processes also lead to a dimer crystallization at some order of the perturbation theory. A similar analysis may be performed individually for a given lattice.

Experimental systems.— The considered model and the derived results may be relevant for several experimentally studied materials.

In the layered compound NaTiO_2 [10, 11] the spin one-half Ti^{3+} ions form a triangular lattice and have one d -electron in the three-fold degenerate t_{2g} manifold (d_{xy} , d_{xz} , and d_{yz} orbitals). The three non-equivalent bonds of the triangular lattice are aligned along the xy , xz , and yz directions, and each orbital state has a dominant hopping amplitude along the corresponding bond. This system does not show any signature of long-range magnetic order at low temperatures [10]. A drop of magnetic susceptibility has been observed [11], but no dimerized superstructure has yet been detected.

The compound Sr_2VO_4 is a possible realization of the

model (1) on the square lattice (formed by spin one-half Vanadium ions). Each V^{4+} ion is surrounded by the distorted oxygen octahedra elongated in the z -direction [12] and single d electron occupies a two-fold degenerate (d_{xz} and d_{yz}) level. On the square lattice in the xy plane, the d_{xz} and d_{yz} electrons hop only in the x and y directions, respectively. The experimental study of $Sr_2VO_{4-\delta}$ [13] suggested an absence of magnetically ordered states down to zero temperature and a possible formation of singlet pairs in the stoichiometric compound $\delta = 0$. The available experimental data are, however, inconclusive about the presence of a spin gap in this compound.

The model (1) on the pyrochlore lattice describes the $MgTi_2O_4$ spinel compound [4]. The latter has a spin gap and a dimerized bond pattern at low temperatures [14]. It has been shown in Ref. [4], within the mean-field like approach, that the dimer states for model (1) on a pyrochlore lattice are favorable over some other magnetic states. Here we provide a proof that dimer states are the ground states. Our mechanism of the selection of VBC pattern would, however, predict a different dimer pattern than observed experimentally in $MgTi_2O_4$. This suggests that in this compound the degeneracy is lifted by a magnetoelastic mechanism, as discussed in Ref. [4], and not by quantum fluctuations. An alternative mechanism for observed dimerized pattern within a different (itinerant-electron) model has recently been suggested in Ref. [15].

Note that our model has two different energy scales. At the higher energy scale (of order J), the system organizes into classically fluctuating singlets (dimers). This possibly explains the spin gap in the compounds mentioned above. The crystallization of dimers by triplet fluctuations occurs at a much lower energy scale (determined by the ηJ term in Eq. 1). In real systems, this is one of several possible mechanisms of crystallization (including magnetoelastic effects, residual overlaps between orbitals in non-dominant directions, etc.) For any particular compound, a theoretical prediction of the crystallization pattern would require a thorough analysis of different ordering mechanisms. On the experimental side, an identification of the dimerization pattern may be difficult in the case of large unit cells like those predicted in this work.

Summary.— To summarize, we have studied a spin-orbital model for a family of quantum antiferromagnets with orbital degeneracy. In such systems, the orbital degrees of freedom induce a spontaneous dimerization of the spins. The resulting extensively degenerate ground state is equivalent to a problem of constrained classical hard-core dimers. At a lower energy scale, the extensive degeneracy is lifted through an order-out-of-disorder mechanism by virtual triplet excitations and a valence-bond crystal is formed. At intermediate temperatures, above the dimer crystallization, the spin system is in a

liquid state. Our study proposes a mechanism of the spin-gap formation experimentally observed in several two- and three-dimensional systems. An interesting possible extension of our model may include additional terms arising from neglected overlaps of orbitals and leading to a quantum dynamics of dimers. Such an extension might be a better candidate than pure spin systems for a realization of quantum dimer models [16, 17] and of the long-sought quantum spin-liquid phase.

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